

Standard Operating Procedure for the
Digestion of Aqueous and Solid Samples
Using Method 200.2 Hot Block Digestion Technique

Method 200.2 (Hot Block, Water and Soil/Sediment)

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TABLE OF CONTENTS

	PG
1. SCOPE AND APPLICATION	3
2. HEALTH AND SAFETY	4
3. SUMMARY OF METHOD	5
4. DEFINITIONS	5
5. CAUTIONS	5
6. INTERFERENCES	6
7. EQUIPMENT AND SUPPLIES	6
8. REAGENTS AND STANDARDS	7
9. SAMPLE COLLECTION, PRESERVATION AND STORAGE	8
10. PROCEDURE	9
11. QUALITY CONTROL	14
12. PREVENTATIVE MAINTENANCE AND TROUBLESHOOTINGh	14
13. POLLUTION PREVENTION AND WASTE HANDLING	14
14. CALCULATIONS AND DOCUMENTATION	15
15. LIMS ENTRY AND REPORTING	15
16. REFERENCES	16
Appendix	16

1. SCOPE AND APPLICATION

- 1.1. This method provides sample preparation procedures for the determination of total recoverable analytes in groundwaters, surface waters, drinking waters, wastewaters, and, with the exception of silica, in solid type samples such as sediments, sludges and soils. Aqueous samples containing suspended or particulate material $\geq 1\%$ (W/V) should be extracted as a solid type sample. This method is applicable to the following analytes:

<u>Analyte</u>		<u>Chemical Abstract Services Registry Number (CASRN)</u>
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Boron	(B)	7440-42-8
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Cerium	(Ce)	7440-45-1
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Lithium	(Li)	7439-93-2
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Phosphorus	(P)	7723-14-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silica	(SiO ₂)	7631-86-9
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Thorium	(Th)	7440-29-1
Tin	(Sn)	7440-31-5
Uranium	(U)	7440-61-1
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

Please note: This method is not suitable for the determination of silica in solids.

- 1.2. For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest Federal Register announcement.
- 1.3. Samples prepared by this method can be analyzed by the following methods given in this supplement: Method 200.7, Determination of Metals and Trace Elements by Inductively Coupled Plasma-Atomic Emission Spectrometry; Method 200.8, Determination of Trace Elements By Inductively Coupled Plasma-Mass Spectrometry; and Method 200.9, Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry
- 1.4. This method is suitable for preparation of aqueous samples containing silver concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well-mixed aliquots must be prepared until the analysis solution contains <0.1 mg/L silver. The extraction of solid samples containing concentrations of silver >50 mg/kg should be treated in a similar manner. Also, the extraction of tin from solid samples should be prepared again using aliquots <1 g when determined sample concentrations exceed 1%.
- 1.5. This method will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.
- 1.6. Detection limits and reporting limits and uncertainty are given in the analytical SOP.

2. HEALTH AND SAFETY

- 2.1. Most metallic elements are toxic. Handle with care.
- 2.2. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.
- 2.3. Material safety data sheets for all chemical reagents should be available to and understood by all personnel using this method. Specifically, concentrated hydrochloric acid and concentrated nitric acid are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses, gloves and a lab coat to aid in preventing analyst exposure when working with these reagents.

- 2.4. Disconnect the mains (ie. building power) hot block power cord before making or breaking connections. Use hot block in a validated, operating fumehood.
- 2.5. The hot block surfaces are hot during, and for a period of time, after use.

3. SUMMARY OF METHOD

- 3.1. Solid and aqueous samples are prepared in a similar manner for analysis. Nitric and hydrochloric acids are dispensed into a hot block digestion vessel containing an accurately weighed or measured, well-mixed, homogeneous aqueous or solid sample. Aqueous samples are reduced in volume by gentle heating, and metals and toxic elements are extracted from either solid samples or the undissolved portion of aqueous samples by refluxing the sample in the acid mixture. After digestion, the solubilized analytes are diluted to specified volumes with ASTM Type I water, mixed, centrifuged if required, and removed from solid precipitate immediate after centrifuging before analysis. Digested samples are to be analyzed by the appropriate mass and/or atomic spectrometry methods as soon as possible after preparation.

4. DEFINITIONS

- 4.1. Solid Sample: For the purpose of this method, a sample taken from material classified as either soil, sediment or sludge.
- 4.2. Total Recoverable Analyte: The concentration of analyte determined to be either a solid sample or an unfiltered aqueous sample following treatment by refluxing with hot dilute mineral acid.
- 4.3. Water Sample: For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial, or domestic waste water.
- 4.4. Dissolved Metal Samples: Samples filtered through a 0.45 µm filter in the field.
- 4.5. LCS (Laboratory Control Standard): A known reference material which is processed as a sample to monitor digestion and analytical performance.
- 4.6. SRM (Standard Reference Material): A known solid reference material which is processed as a sample to monitor sediment digestion and analytical performance
- 4.7. Temperature Blank: A digestion vessel filled with de-ionized water to be used to measure working temperature of the hot block. This temperature is recorded in instrument log book and bench sheet.

5. CAUTIONS

- 5.1. Due to vial breakage with the screw-cap tubes, centrifugation should be limited to 1000 rpm. Higher speeds up to 2000 rpm may be used with snap-top tubes.

6. INTERFERENCES

- 6.1. In sample preparation, contamination is of prime concern. The work area, including bench top and fume hood, should be periodically cleaned in order to eliminate environmental contamination.
- 6.2. Chemical interferences are matrix dependent and cannot be documented previous to analysis.

7. EQUIPMENT AND SUPPLIES

- 7.1. Analytical balance, Mettler Toledo AG 285 or equivalent, with capability to measure to 0.1 mg, for use in weighing solids, and for determining dissolved solids in extracts.
- 7.2. Temperature adjustable hot block digester such as Environmental Express, CPI ModBlock™, or equivalent, capable of maintaining a temperature of 95 °C.
- 7.2.1. 50 mL High Density Polyethylene (HDPE) digestion vessels with either snap-on caps or screw caps and ribbed watch glasses. Each lot of digestion vessels comes with a certificate of volume which is currently kept in room 1024.
- 7.3. Centrifuge, Beckman Allegra 6 or equivalent.
- 7.3.1. Please note: Centrifuge to be used with caution. See 5.1.
- 7.4. A gravity convection drying oven with thermostatic control capable of maintaining 105 ± 5 °C, Lab-Line Imperial V or equivalent
- 7.5. Impact grinder, Chemplex SpectroMill I or equivalent, with polystyrene grinding vessels and methacrylate impact balls or ceramic or nonmetallic mortar and pestle.
- 7.6. NIST-traceable thermometer, accuracy ± 1 °C, within hot block operation range.
- 7.7. Wash bottle - One piece stem, Teflon FEP bottle with Tefzel ETFE screw closure.
- 7.8. Glassware and Plasticware
- 7.8.1. Volumetric flasks, 100 mL: glass Class A, (± 0.08 mL) or polypropylene Class B (± 0.16 mL)
- 7.8.2. Other volumes as required for dilutions

- 7.8.3. HDPE digestion vessels (see 7.2.1).
- 7.8.4. Repipet® dispenser and dilutor, 1% accuracy and 0.1% reproducibility, Barnstead Thermolyne or equivalent
- 7.8.5. 30 mL plastic cups
- 7.8.6. 50 mL centrifuge tubes
- 7.8.7. Eppendorf pipets and tips
 - 7.8.7.1. 50, 100, 200, 250, 500, 1000 $\mu\text{L} \pm 1.0\%$
 - 7.8.7.2. Eppendorf pipets are certified quarterly. Results are kept in log book in ICP laboratory.
- 7.8.8. Glass pipettes, Class A
 - 7.8.8.1. 5 mL ± 0.1 mL
 - 7.8.8.2. Other volumes as required for dilutions
- 7.8.9. Graduated cylinders
 - 7.8.9.1. 10 mL ± 0.2 mL
 - 7.8.9.2. Other volumes as required

8. REAGENTS AND STANDARDS

- 8.1. Reagents may contain elemental impurities which might affect analytical data. High-purity reagents should be used whenever possible. Acids used for this method must be of ultra high-purity grade. For ICP-AES and GFAA, J. T. Baker Instra-analyzed is adequate. Reagents are labeled with LIMS ID and expiration date with grade in comment field.
 - 8.1.1. Nitric acid, concentrated. Expires five years from receipt.
 - 8.1.2. Nitric acid (1+1) -- Add 250 mL conc. nitric acid to 200 mL of ASTM Type I water and dilute to 0.5 L. Solution expires after one year.
 - 8.1.3. Hydrochloric acid, concentrated Expires five years from receipt.

8.1.4. Hydrochloric acid (1+1) -- Add 250 mL conc. hydrochloric acid to 200 mL of ASTM Type I water and dilute to 0.5 L. Solution expires after one year.

8.1.5. Hydrochloric (1+4) -- Add 100 mL conc. hydrochloric acid to 200 mL of ASTM Type I water and dilute to 0.5 L. Solution expires after one year.

8.2. Reagent water -- For all sample preparation and dilutions, ASTM Type I water (ASTM D1193) is required. Suitable water is obtained by passing RO water through a mixed bed of anion and cation exchange resins.

8.3. Refer to the appropriate SOP for the preparation of standard stock solutions, calibration standards, and quality control solutions. Include in LIMS the LIMS IDs of acids used in making standards.

9. SAMPLE COLLECTION, PRESERVATION AND STORAGE

9.1. For determination of total recoverable elements in aqueous samples, the samples must be acid preserved prior to aliquoting for either sample processing or determination by direct spectrochemical analysis. For proper preservation samples are not filtered, but acidified with (1+1) nitric acid to pH <2.

9.2. Dissolved metal samples are those filtered in the field. To ensure matrix matching, dissolved samples are digested.

9.3. Water samples are preserved in the field to a pH<2. Typically 3-5 mL of 1:1 HNO₃ per liter of sample or blank are used. If the sample is not acidified for any reason, especially due to an anticipated hazard, an indication of this condition should accompany the samples and be directed to the attention of the Metals Group Leader. If pH is > 2, either the pH must be adjusted with HNO₃ and time allowed to re-solubilize the analyte(s) that may have adsorbed onto the container walls (24 hr. minimum), or if the sample is extremely basic or highly buffered, and addition of acid would cause precipitation of the analytes of interest, this fact and the pH of the sample must be documented. Date and time and amount of acid added and initials should be recorded on the sample bottle and bench sheet.

9.3.1. Please note: Acidification may release toxic gas and should be done in a fume hood.

9.4. Solid samples require no preservation prior to analysis other than storage at 4 ° C. There is no established holding time limitation for solid samples other than what is recommended by The Office of Solid Waste and Emergency Response (OSWER) in SW846 or required by OSWER for its Contract Laboratory Program (CLP). Water samples are considered stable for six months from date of sampling if properly preserved and stored.

- 9.5. Water and solid samples are kept under refrigeration. Digests are kept at room temperature in a spill tray. Digests are retained for 2-1/2 months after results are reported.
- 9.6. Digests are disposed of in red waste, and containers are single rinsed and disposed of in yellow hazardous waste bags.

10. PROCEDURE

10.1. Aqueous Sample Preparation

- 10.1.1. All digestions require a sample pretreatment log or sample preparation sheet. This requirement is satisfied by the bench sheet generated in LIMS as described in 15.2 below
- 10.1.2. For the determination of total recoverable analytes in aqueous samples, transfer a 50 mL aliquot from a well mixed, acid preserved sample to a 50 mL HDPE digestion vessel that was previously triple rinsed with ASTM Type I water (There is a 50 mL graduation mark on the digestion vessel so that the sample can be transferred directly into the digestion vessel). Label the digestion vessels with Lims ID information. Place each vessel to be digested into the clear plastic hot block carrying rack.
- 10.1.2.1. Please note: At least one digestion blank, spike blank, matrix duplicate and matrix spike must be digested with each digestion batch. Total/dissolved pairs are prepared together, but in separate batches with separate . If more than 10 samples are in the batch, a matrix duplicate and matrix spike will be digested for every 10 samples, or up to 20 samples as determined by the Group Leader. . A method blank and spike blank must be prepared for every 20 samples. Any additional QC samples or additions made to the samples must be conducted according to the appropriate analysis SOP. Any additions to the sample matrix (i.e. matrix spikes) must be made prior to digestion of the sample. Please refer to the appropriate analysis SOP for further information.
- 10.1.2.2. Please note: Include one temperature blank to be used for measuring the working hot block temperature.
- 10.1.3. Add 1 mL (1+1) nitric acid and 0.5 mL of (1+1) hydrochloric acid to all of the digestion vessels containing the sample to be digested. Cover digestion vessels with ribbed watch glasses. Using the clear plastic carrying rack, place the vessels in the hot block for solution evaporation. **DO NOT REMOVE FROM CARRYING RACK.** The hot block should be located in a fume hood.

Please note: Volume of acid delivered can be verified using a 10 mL graduated cylinder.

10.1.3.1. For the CPI ModBlock:

Please note: Disconnect the mains (ie. building power) hot block power cord before making or breaking connections. Use hot block in a validated, operating fumehood, but place the controller outside the hood to avoid corrosion.

10.1.3.1.1. Switch on the system power at the front of the controller. If the AUTO lamp is not lit, press the Auto/Manual button. Press Enter and set the temperature in degrees Celsius with the up and down arrow keys. Press Enter. Set the countdown timer (hours:minutes) and press Enter. The current time will now be displayed; press Enter to start immediately or use the up and down arrow keys for a delayed start.

10.1.3.1.2. If the clock needs to be adjusted, to display the current time (24-hour format), press and hold the Select A/B and Auto/Manual keys. Use the Enter/Start and the Timer keys to adjust the time up or down. Press the up arrow key to return to the main menu.

10.1.3.1.3. For water, set hot block to 97 °C for 9 hours. The timer starts counting down when the system is within 3 °C of the setpoint.

10.1.3.2. For the Environmental Express Hot block:

10.1.3.2.1. The hot block should be plugged into the timer at the outlet, and adjusted to a temperature reading on the hot block of 98 °C to provide evaporation at a temperature of approximately but no higher than 85 °C. All vessels should be placed on the hot block in the carrying rack and covered with a ribbed HDPE watch glass previously triple rinsed with ASTM Type I water.

10.1.3.2.2. Reduce the volume of the sample aliquot to about 10 mL by gentle heating at 85 °C.. This step takes about **9.5 hours for a 50 mL aliquot of sample.**

10.1.3.2.3. Adjust the timer to turn on the hot block on a set day and time and to turn off the hot block **9.5 hours later.**

10.1.4. When hot block has come up to temperature, measure the temperature in the temperature blank using NIST traceable thermometer and record the reading in the instrument log book and bench sheet

10.1.5. Record hot block ID on bench sheet. If a balance was used, record balance number and check weights on bench sheet.

10.1.6. Allow the samples to cool. Rinse the ribbed watch glasses into the digestion vessel using ASTM Type I water. Bring the samples to volume using the 50 mL mark on the digestion vessel with ASTM Type I water. After bringing the samples to volume, securely attach (previously triple rinsed) snap-on covers or screw caps

10.1.7. Mix the sample by inverting and shaking the vessel at least three times.

Please note: If Ag, Mo, Sb, Sn, (and/or possibly Ba) are of interest, then steps 10.1.8 and 10.1.9 must be performed immediately upon finishing step 10.1.7.

10.1.8. If suspended solids are present in the sample, centrifuge the sample at 1000 rpm for one minute or less. (See Section 5.1)

10.1.8.1. Please note: the the centrifuge must be balanced properly before a centrifuge cycle is begun. Please refer to the "Operating Instructions for the Beckman-Allegra 6 Centrifuge."

10.1.9. Remove samples from any particulate matter. If transfer pipet is used, transfer pipet must also be used on a blank.

10.1.10. The samples are now ready for analysis. Because the effects of various matrices on the stability of digested samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

10.1.11. Sample analysis: Use an analytical method listed in Section 1.3.

10.1.12. Digests are to be retained for 2-1/2 months after results are reported.

10.2. Solid Sample Preparation

10.2.1. All digestions require a sample pretreatment log or sample preparation sheet. This requirement is satisfied by the bench sheet generated in LIMS as described in 15.2 below.

10.2.2. For the determination of total recoverable analytes in solid samples, mix the sample thoroughly or withdraw several small subsamples from different parts of the jar and transfer a portion (>20 g) to tared weighing dish, weigh the sample and record the wet weight. (For samples with <35% moisture, a 20 g portion is sufficient. For samples with moisture >35%, a larger aliquot 50-100 g is required.) Dry the sample to a constant weight at 105 °C (or 60 °C if required) and record the dry weight for calculation of percent solids. If sample is very inhomogeneous, a larger subsample can be used.

10.2.3. To achieve homogeneity, grind the dried sample using the Chemplex Impact Grinder. If desired, sieve the sample using a 10-mesh polypropylene sieve. (The sieve should be cleaned using compressed air between samples.) From the dried, ground material weigh accurately a representative 0.5 g aliquot of the sample into a 50 mL HDPE digestion vessel for acid extraction. If high concentrations of some analytes are suspected, a smaller aliquot — typically no smaller than 0.25 g — may be weighed out. Label the digestion vessels with Lims ID information. Record balance ID and check weights on bench sheet and log book.

10.2.3.1. Please note: At least one digestion blank, spike blank, SRM, matrix duplicate, and matrix spike must be digested with each digestion batch. If more than 10 samples are in the batch, a matrix duplicate and matrix spike will be digested for every 10 samples, or up to 20 samples as determined by the Group Leader. A method blank and spike blank must be prepared for every 20 samples. Any additional QC samples or additions made to the samples must be conducted according to the appropriate analysis SOP. Any additions to the sample matrix (i.e. matrix spikes) must be made prior to digestion of the sample. Please refer to the appropriate analysis SOP for further information.

10.2.3.2. Please note: Include one temperature blank to be used for measuring the working hot block temperature.

10.2.4. To each of the digestion vessels add 2 mL of (1+1) HNO₃ and 5 mL of (1+4) HCl. Cover vessels with ribbed watch glasses. Using the clear plastic carrying rack, place the vessels in the hot block for solution evaporation. **DO NOT REMOVE FROM CARRYING RACK.** The hot block should be located in a fume hood.

Please note: Volume of acid delivered can be verified using a 10 mL graduated cylinder.

10.2.4.1. For the CPI ModBlock:

10.2.4.1.1. Switch on the system power at the front of the controller. If the AUTO lamp is not lit, press the Auto/Manual button. Press Enter and set the temperature in degrees Celsius with the up and down arrow keys. Press Enter. Set the countdown timer (hours:minutes) and press Enter. The current time will now be displayed; press Enter to start immediately or use the up and down arrow keys for a delayed start.

10.2.4.1.2. If the clock needs to be adjusted, to display the current time (24-hour format), press and hold the Select A/B and Auto/Manual keys. Use the Enter/Start and the Timer keys to adjust the time up or down. Press the up arrow key to return to the main menu.

10.2.4.1.3. For soil, set hot block to 115 °C for 45 minutes. The timer starts counting down when the system is within 3 °C of the setpoint.

10.2.4.2. For the Environmental Express hot block:

10.2.4.2.1. The hot block should be plugged into the timer at the outlet, and adjusted to a temperature reading on the hot block of 115 °C to provide evaporation at a temperature of approximately but no higher than 95 °C. All vessels should be placed on the hot block in the carrying rack and covered with a ribbed HDPE watch glass previously triple rinsed with ASTM Type I water.

10.2.4.2.2. Adjust the timer to turn on the hot block on a set day and time and to turn-off the hot block **65 minutes later**. 45 minutes of the 65 minutes set on the hot block timer is the digestion time. The other 20 minutes is for warm-up. Very slight boiling may occur during digestion, however vigorous boiling must be avoided to prevent loss of the HCl-H₂O azeotrope. Some solution evaporation will occur (3 - 4 mL).

10.2.5. When hot block has come up to temperature, measure the temperature in the temperature blank using NIST traceable thermometer and record the reading in the instrument log book and bench sheet

10.2.6. Record hot block ID on bench sheet.

10.2.7. Allow the samples to cool. Rinse the ribbed watch glasses into the digestion vessel using ASTM Type I water. Bring the samples to volume using the 50 mL mark on the digestion vessel with ASTM Type I water. After bringing the samples to volume, securely attach (previously triple rinsed) snap-on covers or screw caps and mix the sample by inverting and shaking the vessel at least three times.

Please note: If Ag, Mo, Sb, Sn, (and possibly Ba) are of interest, then steps 10.2.6 and 10.2.7 must be performed immediately upon finishing step 10.2.5.

10.2.8. Samples are centrifuged for one minute or less.

10.2.8.1. Please note: the centrifuge must be balanced properly before a centrifuge cycle is begun. Please refer to the "Operating Instructions for the Beckman-Allegra 6 Centrifuge."

10.2.9. Decant sample into clean tube or withdraw using transfer pipet in order to isolate digestate from remaining solids. The preferred method of decanting is currently under consideration. If transfer pipet is used, transfer pipet must also be used on blank.

- 10.2.10. The samples are now ready for analysis. Because the effects of various matrices on the stability of digested samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.
- 10.2.11. Sample Analysis – Use an analytical method listed in Section 1.3.
- 10.2.12. Digests are to be retained for 2-1/2 months after results are reported.

11. QUALITY CONTROL

- 11.1. The minimum requirements of a QC program consist of an initial demonstration of laboratory capability, and the analysis of digestion blanks, spiked blanks, matrix duplicates and matrix spikes as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data generated.
- 11.2. Digestion QC minimum is a blank and LCS and/or blank spike.
- 11.3. Specific instructions on accomplishing the described aspects of the QC program are discussed in the analytical methods (Section 1.3) and can be found in the applicable analysis SOP.

12. PREVENTATIVE MAINTENANCE AND TROUBLESHOOTING

- 12.1. The digestion vessels, ribbed watch glasses and snap-on caps are all disposable. The hot block and centrifuge should be kept clean and free of contamination from sample spills. All sample spills should be wiped up immediately and the hot block and centrifuge cleaned with water.
- 12.2. All other equipment should be kept clean and free of contamination
- 12.3. Performance of hot block is observed routinely and measured annually by reading temperature in seven randomly spaced tubes. Results are recorded in log book which is kept in Room 1023. Accepted value is $85 \pm 2^{\circ} \text{C}$.
- 12.4. Instrument maintenance logbook documenting maintenance and repair work is located by the hot blocks.

13. POLLUTION PREVENTION AND WASTE HANDLING

- 13.1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation.

- 13.2. The Environmental Protection Agency (EPA) has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.
- 13.3. The EPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations, and the CRL has established color coded "waste streams" to minimize the impact that its operations have on the environment. All nitric/hydrochloric wastes are disposed of in a red labeled waste container. High concentration nitric waste ($\geq 10\%$) and all other strong oxidizing solution wastes are disposed of in an orange labeled waste container
- 13.4. Please see the laboratory chemical hygiene manual for additional information.

14. CALCULATIONS AND DOCUMENTATION

- 14.1. Please refer to analytical SOP's.

15. LIMS ENTRY AND REPORTING

- 15.1. All LIMS data entry is based on first creating a bench sheet describing the sample preparation. This bench sheet describes the samples prepared, and the digestion quality control samples. The spike solution is found in the various instrument SOP's. The analyst must make certain that the preparation date in LIMS matches the actual preparation date. By convention, if the sample preparation proceeds overnight, the date started is used for the LIMS preparation date.
- 15.2. Bench sheet is created under **Laboratory** and then **Batch**. Click **Add**, then choose Department. Choose preparation method and batch matrix and choose the analyses to be analyzed from this batch. Click **Save**. Then go to bench sheet page and select work order number. Click **Edit**. Click **Add**, and then click "Client Samples". Locate the samples in the All Sample Containers dialog, and then right-click to view the shortcut menu. Click Include Selection to insert the selection into the bench sheet dialog. Print bench sheet. If solid samples are digested, the correct weights should be written by hand on the bench sheet and later entered into LIMS in place of the default weights. Verify that the numbers of matrix QCs are correct, or add or delete as appropriate. Choose samples for duplicates or spikes by highlighting and right-click to select "source". Highlight the blank spike and matrix spike(s) and add the spike stock ID QC and spike amounts in microliters. If a solid SRM is used, enter both the correct weight in grams, and the spike amount as the weight in milligrams (*e.g.* if the weight is 0.40 g, enter 400 mg in Spike Amount.) Then click **Save**.
- 15.3. Due to current LIMS constraints, for total/dissolved pairs two batch/bench sheets must be created – one for total and the other for dissolved.

15.4. The bench sheet can be printed from the **Print** menu. Bench sheet is to be initialed and dated with the actual date of prep.

15.5. Reference is made to analytical SOP's for further LIMS information.

16. REFERENCES

- 16.1. Creed, J.T., C. A. Brockhoff, S. E. Long, E. R. Martin, T. D. Martin. Method 200.2 – *Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements*. Environmental Monitoring Systems Laboratory, Office of Research and Development. U.S. Environmental Protection Agency, Cincinnati, Ohio 45268 (1994).
- 16.2. ModBlock™ Instruction Manual, CPI International, 5580 Skylane Blvd., Santa Rosa, CA 95403.

Appendix

Deviation from Method 200.2 Revision 2.8 dated 1994:

1. The use of impact grinder rather than mortar and pestle.
2. Samples are dried at 105 °C since Hg is not analyzed from this preparation.
3. 200.2 is written for hot plate digestion. Private communication with Ted Martin of NRMRL-Cincinnati allows any heating source that can be controlled. And while 200.7 allows that a block digester capable of maintaining a temperature of 95 °C and equipped with 250 mL constricted volumetric digestion tubes may be substituted for the hot plate and conical beakers in the extraction step, 50 mL tubes with watch glasses are used here to allow for reflux.
4. Aqueous samples are not reduced by half but rather returned to original volume.